

Refinement of the Crystal Structure of the Aragonite Phase of CaCO_3

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Aragonite (CaCO_3) crystallizes in the unit cell $a = 4.9598(5) \text{ \AA}$, $b = 7.9641(9) \text{ \AA}$, and $c = 5.7379(6) \text{ \AA}$ at 25°C with four formula weights in space-group $Pmcn$. The structure has been refined to $R_w = 0.024$, $R = 0.040$ using 765 x-ray reflections from a single crystal. The Ca ion is coordinated to nine oxygens with Ca . . . O distances in the range $2.414(2) \text{ \AA}$ to $2.653(1) \text{ \AA}$. The two unique C—O distances in the CO_3 group are $1.288(2) \text{ \AA}$ (on the mirror plane) and $1.283(1) \text{ \AA}$. The two unique O—C—O angles are $119.6(2)^\circ$ (across the mirror plane) and $120.13(8)^\circ$. The distances and angles in the CO_3 group are not significantly different at the 95 percent confidence level.

Key words: Calcium carbonates; carbonates; crystal structure; single crystal x-ray diffraction.

1. Introduction

Aragonite (CaCO_3) is found in nature as a mineral and is an important biomineral because of its presence in coral, clam shells, gallstones, and otoliths. It is isostructural with the carbonates of large divalent cations such as Ba, Sr, and Pb.

Aragonite is less stable than the calcite phase of CaCO_3 at room temperature, transforms into calcite, and is denser than calcite. Thus aragonite is a high pressure form of CaCO_3 . More details are available in reference [1].¹ Because of the importance of aragonite, and because of the possibility of performing calculations on the lattice energies of selected carbonates along the lines suggested by Busing [2], we have collected new x-ray data from a single crystal of aragonite and have refined the structure from the positions given in 1924 by Bragg [3].

2. Structure Determination

Formula (ideal): CaCO_3 (aragonite phase); *Unit Cell*: orthorhombic with $a = 4.9598(5) \text{ \AA}$, $b = 7.9641(9) \text{ \AA}$, $c = 5.7379(6) \text{ \AA}$ at 25°C (calculated by least squares from 12 2θ values observed on a diffractometer; volume: 226.65 \AA^3 ; radiation, $\text{Mo(K}\alpha_1)$, $\lambda = 0.70926 \text{ \AA}$; monochromator: highly oriented graphite crystal; space-group: $Pmcn$; contents $4(\text{CaCO}_3)$; reciprocal lattice extinctions, hkl : $h + k = 2n + 1$, $h0l$: $l = 2n + 1$; observed density, $2.947(2) \text{ g}\cdot\text{cm}^{-3}$ [4]; calculated

density, $2.944 \text{ g}\cdot\text{cm}^{-3}$; *Crystal*: material available was heavily twinned; a small wedge was the largest crystal fragment found which showed no evidence of twinning under optical and x-ray examination; this wedge was attached to thin borate glass fiber with clear household cement; fiber attached to insert in goniometer head with epoxy cement; origin of crystal, mineral sample #75538 from National Museum of Natural History, Smithsonian Institute, Washington, D.C. (Supplied by J. S. White, Jr.); linear absorption corrections made by $8 \times 8 \times 8$ Gaussian quadrature using subroutines written by C. W. Burnham [5] and adapted by B. Dickens; maximum and minimum corrections for absorption = 0.880 and 0.963 (transmission factors). *Intensity Data*: number of reflections, 2356 collected from 3 octants and merged into a unique set of 765, of which 619 are "observed" and 146 are "unobserved"; unobserved reflections are those less than 2σ above background; maximum $\sin \theta/\lambda$ for data 0.907 \AA^{-1} ; method used to estimate data: θ - 2θ scan, scintillation counter; diffractometer: Picker² 4-circle single-crystal diffractometer automated by PDP 8/I computer through FACS-1 interface and adapted to include least significant digit of counts; *Computation*: setting programs, those of reference [6] as adapted by Picker Nuclear Corporation; scan range: $1.4^\circ + 114.6 \frac{\Delta\lambda}{\lambda}$, $\Delta\lambda = 0.692$, $\lambda = 0.70926 \text{ \AA}$; scan parameters: backgrounds counted at higher and lower 2θ for 100 s each; θ - 2θ scan at

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¹ Figures in brackets indicate the literature references at the end of this paper.

²Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

0.25°/min for 2θ from one background position to the other; attenuators: 00.25 mm thick layers of Nb, 2 layers for first attenuator, 4 for second, 6 for third; scan range correction: table look-up method to obtain values recommended in reference [7]; intensity data on paper tape, processed by program written by B. Dickens for Univac 1108 computer; this program contains adaptations of subroutines written for similar program by F. A. Mauer (NBS), standard reflection plotting routine and extinct reflection editing routine from programs by J. M. Stewart, University of Maryland, and uses an intense standard reflection (at low 2θ angle) measured every 50 reflections to correct for any change in intensity of the primary x-ray beam. Counts in peak = $I = P - (T/2T_B)(B_L + B_H)$, $\sigma(I) = [P + (B_L + B_H)(T/(2T_B))^2]^{1/2}$, $F = [(AF)(LP)(I)]^{1/2}$, $\sigma(F) = (\sigma(I)/2)(LP/I)^{1/2}$, $LP = 2 \sin 2\theta_c / (\cos^2 2\theta_m + \cos^2 2\theta_c)$, $\beta = -1.58883 \times 10^6 [\lambda^2 (\cos^2 2\theta_m + \cos^4 2\theta_c) dA/d\mu] / [AV^2 \sin^2 \theta_c (\cos^2 2\theta_m + \cos^2 2\theta_c)]$ (for extinction corrections, calculated at same time as absorption correction). P = counts at the peak position, B_L and B_H = background counts at lower and higher 2θ respectively, T = time spent counting peak, T_B = time spent counting each background, AF = attenuator factor, LP = Lorentz-polarization correction, θ_c = Bragg angle for reflection under consideration, θ_m = Bragg angle for monochromator (= 6.005° here), A = transmission factor in the absorption correction, μ is the linear absorption coefficient, $dA/d\mu$ is in mm, V is the volume of the unit cell in Å³. Data merging program for equivalent reflections, written by B. Dickens for Univac 1108 computer; in this program each set of equivalent reflections is treated as follows: Reflections which were all unobserved were averaged and given the largest individual standard deviation in the set. Unobserved reflections in the presence of at least one observed reflection were discarded. Observed reflections which occurred only once in the reflection list subsequent to this step were copied unchanged but their standard deviations were increased by a factor of three. Observed reflections with magnitudes which agreed within the counting statistics and reflections with magnitudes whose ratios fell within the range 0.95 to 1.06 were averaged and given as standard deviation the maximum of the standard deviation from counting statistics and the standard deviation from the range estimate [8, 9]. Under these circumstances, reflections whose magnitudes did not pass the criteria were discarded. If no members of a set of equivalent reflections passed the criteria, the highest magnitude was taken and the associated standard deviation multiplied by five. The justification for these arbitrary increases of standard deviation is that, without some corroboration, every reflection is suspect because of the possibilities of multiple reflection, including the "tail" of nearby intense reflections in its measurement, change in intensity of x-ray beam during reflection measurement, misalignment of crystal, etc. Since we usually measure three sets of equivalent reflections with care the number of standard deviations increased in this way is very small. Scattering factors: those for the neutral atoms in reference [10]; least-squares refinements:

full-matrix, with $\sum w(|F_o| - |F_c|)^2$ minimized; refinements include unobserved reflections which calculate higher than 2σ above background; least-squares weights: $1/\sigma^2(F)$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; thermal parameters have the form $\exp [-1/4(a^*B_{11}h^2 + b^*B_{22}k^2 + c^*B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$. Most least squares and electron density synthesis calculations were carried out with the X-ray 67 system [11] of computing programs.

Final Refinement: $R_w = 0.024$; $R = 0.040$, average shift/error for last cycle = 0.0017; standard deviation of an observation of unit weight

$$= [\sum w(F_o - F_c)^2 / (765 - 28)]^{1/2} = 0.775.$$

The structure was refined isotropically from the positions given by Bragg to $R_w = 0.031$, $R = 0.047$, and then anisotropically to $R_w = 0.024$, $R = 0.040$. The low value of R_w supports the earlier indications that the crystal used in the data collection is not twinned. The highest peak in an electron density difference synthesis calculated after anisotropic refinement to $R_w = 0.024$ corresponded to about 1/3 of an electron and was about 0.95 Å from C towards O(1). The largest correlation coefficients are 0.34–0.44 between the scale factor and the B_{11} , B_{22} and B_{33} temperature factors of Ca.

Two cycles of least squares refinement in which the isotropic secondary extinction parameter r in $F^2 = F_{\text{unc}}^2 / (1 + \beta r |F_{\text{unc}}|^2)$ was varied [12] together with all other unconstrained parameters resulted in no change in R_w or R and gave a value of $-0.3(9) \times 10^{-8}$ for the extinction parameter. There was no significant change in the structural details or their standard deviations. Thus, we believe secondary extinction to be negligible in our crystal of aragonite. Only the observed reflections were used in these refinements. Three cycles of least squares refinement in which allowance was made for the anomalous scattering of Ca (values taken from reference 10) gave an increase from 0.024 to 0.025 for R_w . R was unchanged. There were no significant changes in the atomic positions.

The atomic parameters from the refinements without corrections for anomalous dispersion are given in table 1. The observed and calculated structure factors are given in table 2. The thermal parameters from the refinements which included corrections for the anomalous scattering of Ca are Ca: 0.71(1), 0.65(1), 0.65(1), 0.00, 0.00, $-0.01(1)$; C: 0.67(5), 0.80(6), 0.43(5), 0.00, 0.00, 0.08(5); O(1): 1.45(5), 0.51(4), 1.01(5), 0.00, 0.00, 0.04(5); O(2): 0.67(3), 0.98(3), 1.00(3), $-0.32(3)$, $-0.02(3)$, $-0.09(3)$. Only those for Ca are significantly different from the values in table 1. Distances and angles referred to in the paper were calculated using the values in table 1.

3. Description of the Structure

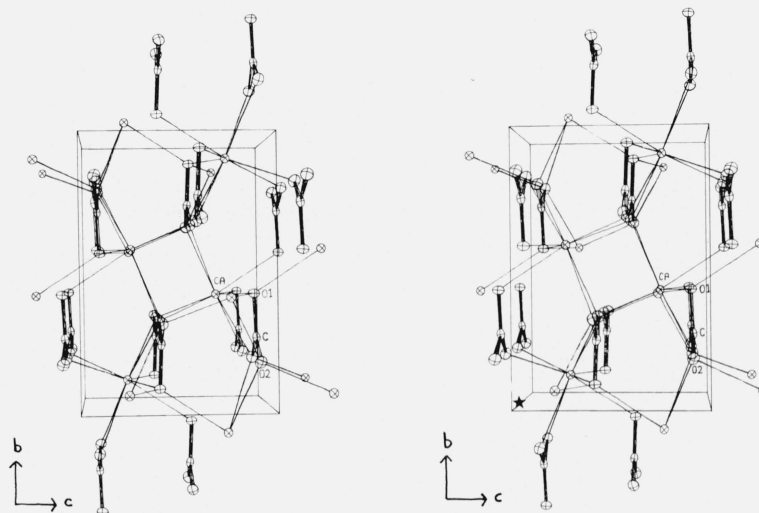
The structure of aragonite, the main points of which are well known, is shown in figure 1. The Ca ions lie in pseudohexagonal layers parallel to (001) and the layer sequence is ABAB. The Ca layers are separated by CO₃ groups which lie in two layers parallel to (001), and form columns parallel to [001].

TABLE 1. Atomic parameters in aragonite (CaCO_3)

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁ *	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Ca	0.25000	0.58507(5)	0.25974(6)	0.664(9)	0.599(9)	0.601(9)	0.0000	0.0000	−0.01(1)
C	.25000	.2386(2)	.4148(3)	.75(5)	.85(5)	.46(5)	.0000	.0000	.07(5)
O(1)	.25000	.0770(2)	.4043(2)	1.50(5)	.54(4)	1.04(4)	.0000	.0000	.03(4)
O(2)	.4737(2)	.3196(1)	.4131(2)	0.71(3)	1.03(3)	1.02(3)	−0.32(3)	−.02(3)	−.09(3)

Figures in parentheses are standard errors in last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinement.

*Thermal parameters are in \AA^2 .

FIGURE 1. A stereoscopic illustration of the crystal structure of aragonite (CaCO_3).

A unique set of atoms is labeled. The origin of the crystallographic coordinate system is marked by *.

3.1. The Ca Ion Environments

The Ca ion lies on the mirror plane at $x=1/4$. Its environment is shown in figure 2 and summarized in table 3. The coordination of nine oxygens to Ca consists of three CO_3 edges, O(1, 2), O(1', 2') and O(2^{IV}, 2^V) and three apexes, O(1^{II}, 2^{II}, 2^{III}). The apparent thermal motion of Ca is almost isotropic (table 1, fig. 2).

Corrections as given by Busing and Levy [13] to obtain the mean separation between atoms from the observed atomic positional and thermal parameters were calculated using a program written by Finger [12]. These corrections are included in tables 3 and 4.

3.2. The CO_3 Group

The details of the CO_3 group and its environment are given in table 4 and shown in figure 3. The positions reported by Bragg [3] give C–O distances of 1.26 Å and 1.30 Å, and O–C–O angles of 117°, 117° and 127°, which, under the circumstances, are all close to those reported here. The C–O distances and O–C–O angles reported here for the CO_3 group do not differ from each other significantly at the 95 percent confidence level; the same is true for the O–C–O angles. In view of the possibility of unknown systematic error, necessarily excluded from the calculations, our results

therefore do not preclude trigonality of the CO_3 group. Because the oxygens in the CO_3 group have very similar environments, little deviation from trigonality is expected. The CO_3 group is nonplanar however. The carbon atom is 0.026(4) Å out of the plane of the oxygen atoms in the CO_3 group in aragonite. This displacement is approximately seven times the standard deviation and is clearly significant. The displacement is towards the nearest Ca layer and is presumably a result of polarization of each oxygen atom by the three bonded Ca ions. If the displacement were caused by Ca . . . C interactions, the C atom would not move towards the Ca layer.

The difference in the O–C–O angles, 119.6° and 120.13°, if real, is consistent with the O(2, 2') edge of the CO_3 group being coordinated slightly more strongly to Ca as judged from the Ca . . . O distances. However, this stronger coordination of O(2) to Ca would also suggest that C–O(2) should be longer than C–O(1). This is not the case. The average value of the C–O distances is 1.286 Å. This agrees well with the C–O distances of 1.283(2) Å reported [14] for calcite in which 32 symmetry is forced on the CO_3 group by space-group R3c. If the apparent thermal motions of the atoms in the CO_3 group are attributed to thermal motion rather than to slight positional disorder, there

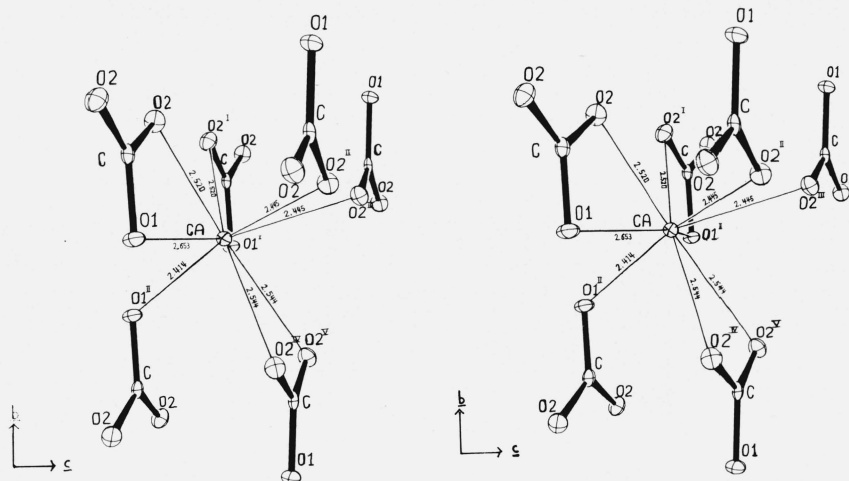


FIGURE 2. The Ca environment in aragonite (CaCO_3).

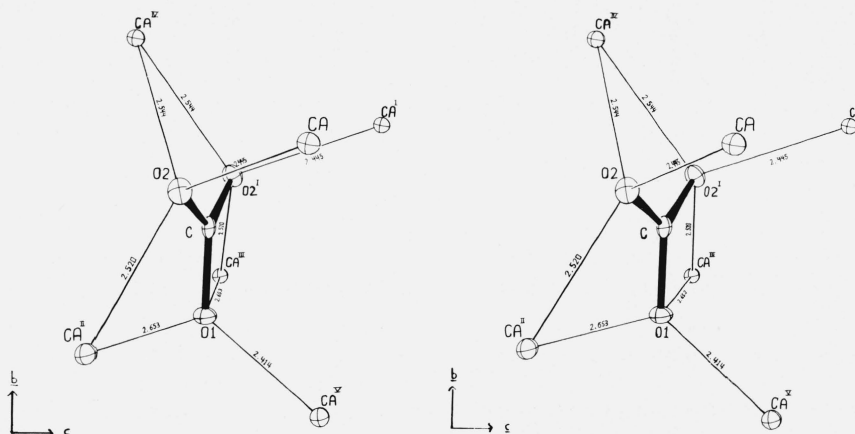


FIGURE 3. The CO_3 group environment in aragonite (CaCO_3).

The labels refer to atoms in table 4.

seems to be oscillation within the CO_3 layer, i.e., more or less perpendicular to the edge coordination to Ca.

Similarly, O(1) may be undergoing some additional wagging out of the CO_3 layer.

TABLE 3. The Ca environment in aragonite (CaCO_3)

Atoms	Distance, Å raw	*Lower bound [13]	*Noncorrelated motion [13]
Ca, O(1 ^{II})	2.414(2)	2.414	2.423
Ca, O(2 ^{II} , 2 ^{III})	2.445(1)	2.445	2.454
Ca, O(2, 2 ^I)	2.520(1)	2.520	2.527
Ca, O(2 ^{IV} , 2 ^V)	2.544(1)	2.544	2.551
Ca, O(1, 1 ^I)	2.653(1)	2.653	2.660

In all tables of interatomic distances and angles, the figures in parentheses are standard deviations in the last digit and were calculated from the standard deviations in the atomic positional parameters and the unit cell parameters.

*Mean separation between atoms when allowance is made for thermal motion.

TABLE 4. The CO_3 group and its environment in aragonite (CaCO_3)

Atoms	Distance, Å or angle, deg.	Lower bound [13]	Riding model [13]
C, O(1)	1.288(2) Å	1.289 Å	1.295 Å
C, O(2)	1.283(1)	1.284	1.288
O(1), O(2)	2.229(1)		
O(2), O(2 ^I)	2.219(2)		
O(1), C, O(2)	120.13(8)°		
O(2), C, O(2 ^I)	119.6(2)		
O(1), Ca ^V	2.414(2) Å		
O(1), (Ca ^{II} , Ca ^{III})	2.653(1)		
O(2), Ca	2.445(1)		
O(2), Ca ^{II}	2.520(1)		
O(2), Ca ^{IV}	2.544(1)		

Table 2. Observed and calculated structure factors for aragonite (CaCO₃)₃

0.K.10	5 47 45	0.K.9	5 363 365	10 46 42	6 186 -184	10 57 47	3.K.2	4 41 39	2 203 -202	4.K.7	2 42 -43	6.K.0	6 28* 6	3 175 -165
2 30 -61	7 21* 14	1 70 64	6 18* -3	1.K.8	8 156 -157	11 30* -30	0 120 -122	6 47 45	4 161 159	1 61 -69	4 48 -48	0 257 -256	7 89 84	4 54 -51
4 298 -289	4 22* -28	2 147 -150	8 44 53	1.K.7	9 65 -69	2.K.7	1 206 -204	7 24* -18	5 21* 16	2 152 146	5 258 263	2 128 -131	8 129 -127	5 113 -116
6 303 -357	4 103 -109	3 47* -16	9 47 -43	0 181 -187	10 146 148	2 74 -73	2 74 -73	8 27* 18	9 234 236	3 44 41	6 23* -1	4 83 85	6.K.6	7 132 122
8 204 -268	10 113 110	4 28 -44	10 42 40	1 117 110	11 46 42	1 34 26	3 360 360	9 164 -162	7 46 43	4 101 191	7 224 213	4 300 299	0 186 174	7.K.5
10 140 142	11 64 -66	5 37 -52	11 150 -157	2 47 -20	12 160 155	2 252 -253	4 19* -25	10 48 -28	8 61 58	5 27* 23	8 54 59	8 28* 24	1 29* 32	1 115 -112
12 265 284	12 100 98	6 27* 0	12 25* 3	3 143 146	13 39 36	3 72 66	5 200 204	3.K.7	10 100 -101	7 80* 34	10 27* 26	10 60 -45	2 91 79	1 115 -112
14 42 20	15 49 69	7 46 -38	13 184 -178	4 36 27	5 80 81	2.K.3	5 116 -118	7 194 -196	11 28* -36	8 152 -152	11 77 -83	6.K.1	3 60 67	2 31* 28
0.K.1	0.K.5	0.K.10	1.K.4	6 135 133	6 27* -28	8 23* -21	1 107 114	2 119 120	12 160 -117	4.K.8	5.K.4	1 47 43	5 29* 37	4 82 -77
1 20 21	1 96 96	0 48 -36	0 96 85	7 85 -89	1 33 29	7 27* -22	9 198 -198	3 24* 19	4 43 46	0 115 116	0 88 83	3 56 -51	6.K.7	7.K.6
2 472 -469	2 224 -223	1 109 -110	1 290 287	8 28* 37	2 46 -50	8 146 152	10 23* 9	5 150 -150	1 44 -34	1 61 -53	1 193 195	4 157 161	1 29* 32	1 115 -112
3 335 -344	3 133 134	2 88 -85	2 84 -82	9 111 -111	3 18* 10	9 28* 23	11 90 -87	6 26* 22	2 200 272	2 100 97	2 92 -88	5 42 41	1 49 30	0 48 -46
4 634 -655	4 283 -286	3 58 -52	1 163 365	1.K.9	5 38 -44	4 391 -393	10 149 147	7 79 -87	3 21* 10	3 60 91	3 217 211	6 24* 17	2 152 -151	1 73 80
5 230 228	5 200 -199	4 61 75	4 61 75	1.K.8	6 126 129	2.K.8	8 146 152	10 23* 9	4 43 46	4 43 46	4 43 46	4 43 46	3 46 25	2 30* -16
6 47 46	6 24* 31	5 193 189	1 145 145	7 21* -24	2 95 93	8 177 180	0 180 -180	1 418 423	5 22* 22	5 22* 22	5 22* 22	5 22* 22	3 126 124	3 126 124
7 60 72	7 126 -126	1 54 -61	7 157 -160	2 95 93	8 177 180	0 180 -180	1 418 423	2 72 76	6 26* 22	6 26* 22	6 26* 22	6 26* 22	3 126 124	3 126 124
8 300 324	8 212 208	3 464 477	8 23* 17	5 126 -129	11 26* 21	3 63 -70	3 102 -99	4 97 103	8 68 -70	8 68 -70	8 68 -70	8 68 -70	3 126 124	3 126 124
9 73 -75	9 61 63	5 464 477	8 23* 17	5 126 -129	11 26* 21	3 63 -70	3 102 -99	4 97 103	8 68 -70	8 68 -70	8 68 -70	8 68 -70	3 126 124	3 126 124
10 153 151	10 113 108	3 464 477	8 23* 17	5 126 -129	11 26* 21	3 63 -70	3 102 -99	4 97 103	8 68 -70	8 68 -70	8 68 -70	8 68 -70	3 126 124	3 126 124
11 79 80	11 26* -11	9 731 -129	10 42 -44	6 43 3	12 38 -18	5 53 52	5 221 -224	1 82 -85	10 164 -170	1 62 54	10 29* -28	6.K.2	1 124 -122	0 247 235
12 40 33	12 26* -11	9 731 -129	10 42 -44	6 43 3	12 38 -18	5 53 52	5 221 -224	1 82 -85	10 164 -170	1 62 54	10 29* -28	6.K.2	1 124 -122	0 247 235
13 00 -77	13 22* -5	12 25* 7	1.K.10	2.K.4	6 113 117	6 21* 3	2 51 43	11 27* -26	2 111 -117	2 111 -117	2 111 -117	2 111 -117	3 177 -172	2 47 42
14 161 -159	14 22* -5	12 25* 7	1.K.10	2.K.4	6 113 117	6 21* 3	2 51 43	11 27* -26	2 111 -117	2 111 -117	2 111 -117	2 111 -117	3 177 -172	2 47 42
0.K.2	0.K.6	1.K.1	1.K.5	0 47 42	0 338 -336	1 18* 8	2.K.9	10 47 -38	6 151 -153	4.K.4	5.K.0	1 177 177	3 123* 123	8.K.1
1 206 -210	2 22* -13	1 423 421	1 257 249	2 63 66	2 94 -86	3 118 -119	3 116 -117	1 50 -50	11 179 184	7 96 94	0 121 119	1 44 -45	4 39 -29	5 75 -62
2 409 -401	4 111 -111	3 51 -49	3 20* -14	4 176 182	2 56 52	3 116 -117	1 50 -50	11 179 184	7 96 94	0 121 119	1 44 -45	4 39 -29	5 75 -62	7.K.1
3 308 -309	5 51 51	4 175 168	4 20* 0	5 167 -168	3 37 -38	3.K.4	3.K.4	3.K.4	3.K.4	3.K.4	3.K.4	3.K.4	3.K.4	3.K.4
4 208 234	5 214 214	5 300 -300	5 218 -216	6 116 117	4 156 153	5 72 65	0 38 33	1 183 -187	2 40 -39	3 35 30	7 131 -134	5 53 -54	7 26* -17	2 44 -39
5 104 -5	7 44 35	6 204 33	6 22* -31	0 469 -494	7 163 162	8 59 -51	1 168 -169	3 44 35	6 132 -136	6 132 -136	6 132 -136	6 132 -136	6 132 -136	6 132 -136
6 344 346	8 136 140	7 192 -187	7 158 -162	4 151 146	9 24* 3	6 116 117	4 156 153	5 72 65	0 38 33	1 183 -187	2 40 -39	3 35 30	7 131 -134	5 53 -54
7 81 95	8 80 83	8 88 -92	8 23* 4	4 151 146	9 24* 3	6 116 117	4 156 153	5 72 65	0 38 33	1 183 -187	2 40 -39	3 35 30	7 131 -134	5 53 -54
8 62 57	10 48 -92	9 21* 13	9 23* 6	6 615 635	10 127 -129	4 74 -77	3.K.10	3 305 -303	5 89 92	8 48 -35	9 61 -80	1 224 225	0 48 41	2 98 -102
9 55 -61	11 48 40	10 34 -20	10 45 -34	8 21* 4	11 54 56	0 106 105	5 191 -191	4.K.0	10 60 89	2 26* -10	1 36 19	3 23* 2	7.K.2	1 50 42
10 133 -124	11 153 152	12 49 -44	12 47 45	12 205 -201	10 71 -71	12 135 -130	2 44 37	6 59 56	11 49 -46	3 50 -57	4 113 119	2 25* 30	4 201 -191	2 85 -89
11 57 -59	0.K.7	12 49 -44	12 47 45	12 205 -201	10 71 -71	12 135 -130	2 44 37	6 59 56	11 49 -46	3 50 -57	4 113 119	2 25* 30	4 201 -191	2 85 -89
12 40 -134	13 91 89	14 47 39	1.K.6	2.K.1	1 201 -202	2 290 292	10 46 46	6 268 -275	1 87 86	8 196 -171	2 175 -177	4 81 -76	6 51 -49	8 105 107
13 56 -69	1 83 -92	2 184 174	1.K.2	0 60 60	2 290 292	10 46 46	6 268 -275	1 87 86	8 196 -171	2 175 -177	4 81 -76	6 51 -49	8 105 107	3 184 179
0.K.3	4 267 251	5 24* 16	0 471 454	2 36 34	2 653 659	4 165 164	3 191 -190	11 87 86	8 196 -171	2 175 -177	4 81 -76	6 51 -49	8 105 107	3 184 179
1 51 -50	6 25* -14	1 407 -404	3 237 -239	3 253 -247	5 22* 10	5 194 33	12 28* 15	10 116 116	3 191 -190	11 87 86	8 196 -171	2 175 -177	4 81 -76	6 51 -49
2 431 489	7 43 37	2 16* -7	4 43 -39	4 270 272	6 23* 17	7 34 22	3.K.5	3.K.5	3.K.5	3.K.5	3.K.5	3.K.5	3.K.5	3.K.5
3 17* 23	3 116 -193	3 476 -471	5 39 -31	5 117 119	7 132 129	9 225 229	1 195 -197	2 40 33	1 19* 4	2 266 -268	9 29* 40	10 110 94	4 101 -97	4 109 107
4 17* -1	9 29* 37	4 16* -10	6 54 -56	6 51 50	8 182 -180	11 39 24	3 21* -19	2 266 -268	9 29* 40	10 110 94	4 101 -97	4 109 107	1 228 211	8.K.4
5 30 30	10 87 -90	5 214 -217	7 86 74	7 90 -85	9 46 37	13 101 -102	3 21* -19	2 266 -268	9 29* 40	10 110 94	4 101 -97	4 109 107	1 228 211	8.K.4
6 13* 16	6 153 -156	6 153 -156	8 23* -15	8 256 -253	10 150 -150	9 46 37	13 101 -102	3 21* -19	2 266 -268	9 29* 40	10 110 94	4 101 -97	4 109 107	1 228 211
7 21* 21	8.K.8	7 181 185	9 152 -152	9 49 -55	11 89 -96	12 48 27	3.K.1	5 220 213	4 335 -340	4.K.1	7 92 -91	8 109 165	9 29* 40	10 110 94
8 112 -113	9 21* 0	8 44 -42	10 38 33	10 227 -230	12 48 27	3.K.1	5 220 213	4 335 -340	4.K.1	7 92 -91	8 109 165	9 29* 40	10 110 94	10 110 94
9 21* 0	9 134 135	9 241 242	11 27* 5	11 47 54	12 28* 28	2.K.6	1 256 -259	6 49 47	5 86 93	6 35 26	7 37 37	8 236 237	1 38 -20	4 9 60
10 230 -222	1 74 -82	10 24* -4	11 28* 14	14 146 144	0 230 230	4 18* 4	5 290 288	10 25* -4	9 60 -43	2 30 -20	4 9 60 -43	2 30 -20	4 9 60 -43	2 30 -20
11 53 -31	2 123 123	11 108 104	12 86 84	13 113 -109	1 146 -142	2 88 -97	2 155 157	6 65 -58	11 120 -123	10 128 129	11 51 56	4 92 79	4 183 186	0 168 -166
12 126 121	3 102 106	12 86 84	13 113 -109	1 146 -142	2 88 -97	2 88 -97	2 155 157	6 65 -58	11 120 -123	10 128 129	11 51 56	4 92 79	4 183 186	0 168 -166
13 27* -11	4 106 -104	13 113 -109	1 146 -142	2 88 -97	2 88 -97	2 88 -97	2 155 157	6 65 -58	11 120 -123	10 128 129	11 51 56	4 92 79	4 183 186	0 168 -166
0.K.4	6 160 -157	7 64 -64	1.K.3	0 515 513	4 72 -69	9 44 43	3.K.6	3.K.6	3.K.6	3.K.6	3.K.6	3.K.6	3.K.6	3.K.6
1 102 103	8 61 -51	9 30* -20	1 510 -505	6 23* -9	2 141 142	6 343 -346	10 54 63	0 64 -64	4.K.2	7 27* 30	8 190 182	11 41 80	2 35 6	1 89 -93
2 308 334	9 30* -20	2 101 -95	3 107 -95	7 88 90	3 61 -58	7 55 -55	11 144 -146	1 88 85	4 106 105	5.K.3	4 30* 26	4 116 119	1 81 -73	2 80 78
3 253 251	4 51 50	4 160 -160	4 83 -82	9 25* -7	5 189 -194	9 62 -71	13 101 -88	3 203 204	1 187 189	1 213 -215	5 52 20	2 25* 1	5 52 20	2 25* 1

Columns are K, 10F_O, 10F_C. F_O and F_C are on an absolute scale. Reflections marked * are "unobserved".

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